

AD-A200 809

1a. REPORT SECURITY CLASSIFICATION		For unlimited distribution and release					
2a. SECURITY CLASSIFICATION AUTHORITY							
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE							
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)					
6a. NAME OF PERFORMING ORGANIZATION University of Lowell		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION			
6c. ADDRESS (City, State, and ZIP Code) University Avenue Lowell, MA 01854				7b. ADDRESS (City, State, and ZIP Code)			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0131			
8c. ADDRESS (City, State, and ZIP Code) Chemistry Division Arlington, VA 22217				10. SOURCE OF FUNDING NUMBERS			
				PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Ordered Thin Films of Polyheterocycles Electrochemical Polymerization and Langmuir-Blodgett Film Formation							
12. PERSONAL AUTHOR(S) T.A. Skotheim, X.Q. Yang, T. Inagaki, L. Samuelsen, S. Tripathy, H.S. Lee, & Y. Okamoto							
13a. TYPE OF REPORT Technical (2)		13b. TIME COVERED FROM 8/87 TO 8/88		14. DATE OF REPORT (Year, Month, Day) October 3, 1988		15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION To be published; Proceedings International Symposium							
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)				
FIELD	GROUP	SUB-GROUP					
19. ABSTRACT (Continue on reverse if necessary and identify by block number)							
Ordering of L-B films of 3-hexadecylpyrrole is investigated using Near Edge X-Ray absorption fine structure (NEXAFS) using synchrotron Radiation and slde with grazing incidence FT-IR spectroscopy.							
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS				21. ABSTRACT SECURITY CLASSIFICATION			
22a. NAME OF RESPONSIBLE INDIVIDUAL				22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL	

Ordered Thin Films of Polyheterocycles
Electrochemical Polymerization and Langmuir-Blodgett Film Formation

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Proceedings, International Symposium on Development of Conducting Organic
Polymers and Ultra Thin Films and Their Use in Electronics
Stockholm, Sweden, November 2-3, 1987

88 11 4, 014

Introduction

The intrinsic anisotropy in electrical and optical properties of conjugated polymeric systems are of fundamental importance in a number of potential technological applications of this class of materials, such as in nonlinear optical systems. Focusing on conjugated polymers at the molecular level has led to considerable advances in the last few years in the synthesis of materials with controlled and predictable ordering.

The development of analytical tools which are sensitive on the molecular scale represent an important contribution to this development, and will be crucial to advance the state of the art to the point where the materials can be tailored to have highly specific electrical and optical properties. In this paper, we discuss some recent work using synchrotron radiation spectroscopy and surface FT IR spectroscopy to study the ordering of thin films of pyrroles and polypyrrroles made by electrochemical oxidation and Langmuir-Blodgett film techniques.

The electrochemical growth processes of thin films of polyheterocycles complexed with a variety of anions have been the subject of several studies (1). The electrochemical growth technique affords many degrees of freedom to influence the growth process, which can lead to materials with widely varying electrical, optical and structural properties (1a,2). In this paper we will discuss how ordering of electrochemically grown thin films can be studied with Near Edge X-ray Absorption Fine Structure (NEXAFS) techniques using synchrotron radiation and also with grazing incidence FT IR spectroscopy. We also report recent results with Langmuir-Blodgett films of 3-hexadecylpyrrole. (1a)



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NEXAFS Spectroscopy

New experimental techniques, which take advantage of the availability of high brightness monochromatized synchrotron radiation, have been developed during the last few years to study the geometry and bond lengths of molecular materials (3). The x-ray absorption fine structure above the absorption edge of a core electron can be divided into a near-edge region (NEXAFS) located within about 30 eV above the edge and an extended region (EXAFS) well above the edge. Both structures result from the scattering processes of emitted photoelectrons which modulate the absorption coefficient. The EXAFS region is well described by a single scattering theory. In the low kinetic energy NEXAFS region intramolecular multiple scattering effects are dominant. The spectrum is dominated by two types of resonances which are referred to as π and σ resonances according to the symmetry of the final state (3). In a molecular orbital picture, the lower-energy π resonances can be considered as resulting from transitions to unoccupied bound states, i.e., antibonding π^* orbitals. The σ shape resonances can be visualized as transitions to anti-bonding virtual σ^* orbitals. Figure 1 shows an energy diagram of the photo-excitation process.

Since the photoabsorption is governed by dipole selection rules, the orthogonality of the π and σ orbitals can be exploited to determine the orientation of an absorbing molecule relative to the surface to which it is adsorbed, by making use of the polarized nature of the synchrotron radiation. For an initial state of σ symmetry we expect the following dependences of the resonance intensities:

$$\sigma \text{ resonance : } I_\sigma \sim \cos^2 \beta,$$

$$\pi \text{ resonance : } I_\pi \sim \cos^2 \gamma,$$

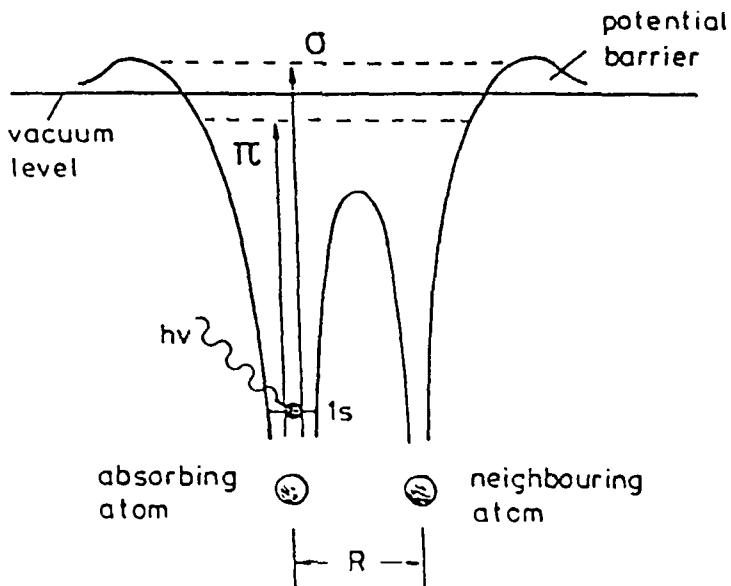


Fig. 1. Core-level photoexcitation to unoccupied π^* and σ^* orbitals in a diatomic molecule.

where β and γ are the angles between the electric field vector of the incident polarized synchrotron light and the σ and π bond directions, respectively.

Surface Infrared Spectroscopy

Complimentary information about the structure and orientation of molecules and thin films on metal surfaces can be obtained with the technique of infrared reflection-absorption spectroscopy (IRRAS). The technique uses grazing incidence reflection from the metal substrate surface. The component of the electric field vector parallel to the reflecting surface undergoes a phase shift of 180° , and consequently, the reflected beam will destructively interfere with the incident beam, producing a node at the surface. The component of the electric field vector polarized essentially normal to the

reflecting surface experiences essentially no phase shift for light incident at small angles. The net result is that, with grazing incident light, only those vibrational modes with a component of the dipole moment normal to the substrate can be detected. With normal incidence transmitted light, on the other hand, only vibrational modes with the dipole moment parallel to the surface are excited. Transmission can be done on transparent substrates, such as Si, or very thin metal films. From the combination the grazing incidence and transmission spectra, it is possible to determine the orientation of well characterized functional groups. This is illustrated schematically in Fig. 2.

The FTIR spectra were taken with a Mattson Cygnus 100 with room temperature DTGS (reflection) and liquid nitrogen cooled MCT (transmission) detectors.

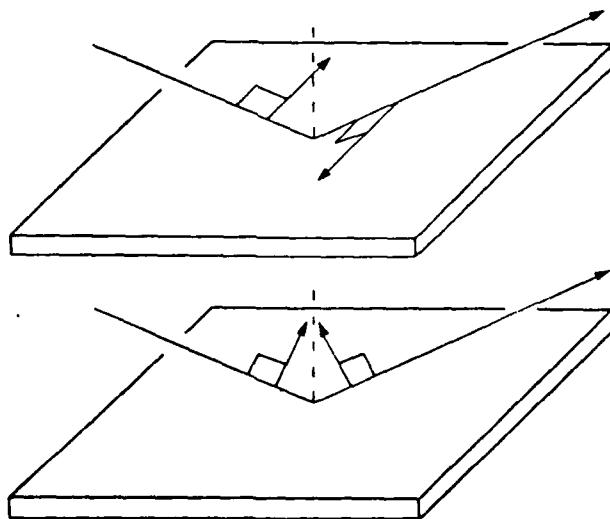


Fig. 2. Electric field vector geometries for transmission and grazing incidence reflection at a metal surface.

Electrochemically Grown Films: Polypyrrole-phthalocyanine

Electrochemically grown polyheterocycles do not exhibit a measurable degree of ordering in the oxidized state when complexed with the usual inorganic anions (e.g., BF_4^- , ClO_4^- , etc.) (4). Thin films (monolayer to $\sim 100\text{\AA}$) of poly(3-methyl thiophene) (PMeT) have been shown to exhibit a high degree of ordering in the reduced, or neutral, state (4b,c). The intercalation of anions during the oxidation process induces disorder resulting in a random average orientation of the thiophene moieties.

One approach to achieve an ordered film in the oxidized and conducting state involves the complexation with sulfonated large, flat macrocyclic anion systems, e.g., sulfonated phthalocyanines (PC), in polypyrrole (2a). Strong π -bonding between the PC and the polypyrrole matrix prevents the electrostatic repulsion of the sulfonated PC molecules. Reduction, therefore, results in a reduced form of the PC as well as the polypyrrole and is accompanied by cation introduction into the film for charge compensation. The film, therefore, cannot be ion free.

Figure 3 shows a NEXAFS spectrum at the carbon K-edge of a 1000\AA film of polypyrrole complexed with Co-PC. The two spectra taken at normal and 20° incident angles show a clear polarization dependence. The $1\text{S} \rightarrow \pi^*$ transition is most pronounced with the electric field vector close to normal to the electrode surface, which implies that the pyrrole rings are oriented predominantly parallel to the electrode surface. This result demonstrates that ordered conducting films can be produced by paying the proper attention to the details of the electrochemical growth process.

Polypyrrole Langmuir-Blodgett Films

A separate approach to a rational design of ordered thin films of polyheterocycles takes advantage of the well-known Langmuir-Blodgett technique to

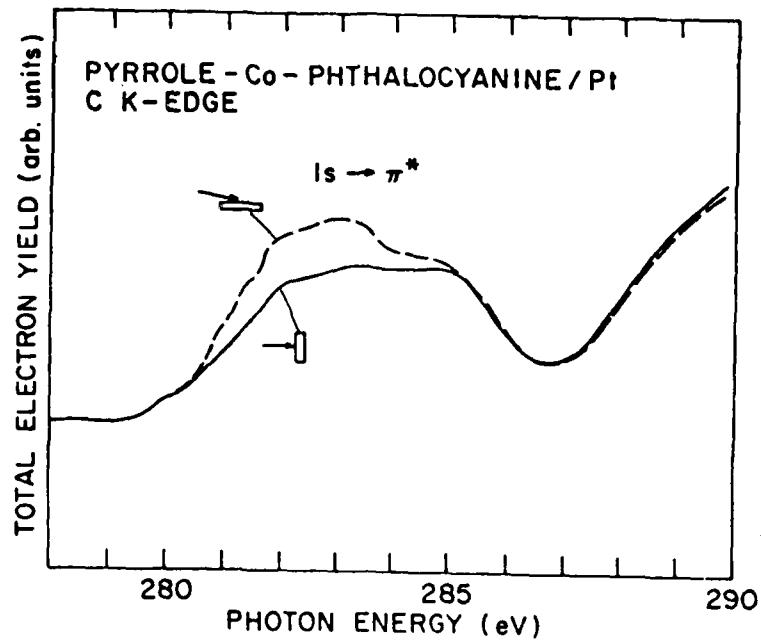


Fig. 3. NEXAFS spectrum at the carbon K-edge for a ~1000 Å thick film of polypyrrole-Co-PC.

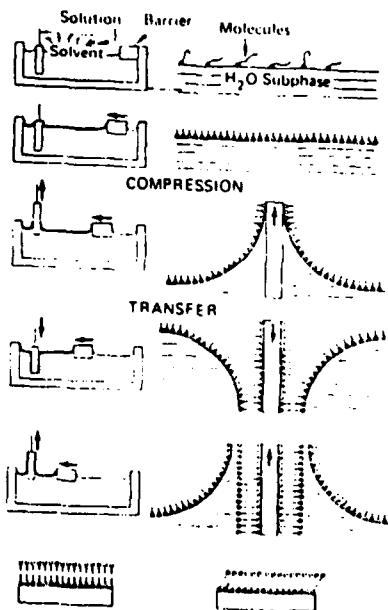
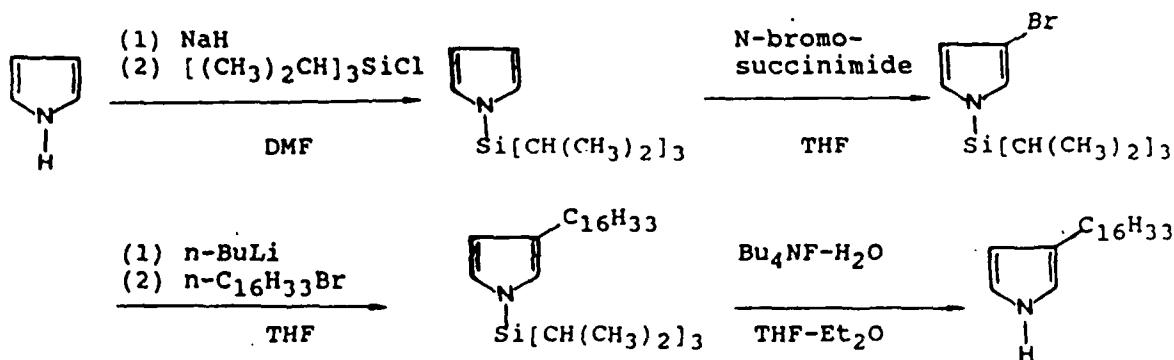


Fig. 4. Schematic diagram of the formation and deposition of Langmuir-Blodgett mono- and multilayer films.

produce what is essentially a two-dimensional structure. This is schematically illustrated in Fig. 4. Coupling Langmuir-Blodgett techniques with electroresponsive molecular and polymeric systems opens new possibilities for design of optically and electrically active interfaces. Here we report on an IRRAS study of 3-n-hexadecylpyrrole Langmuir-Blodgett films on Pt substrates.

The synthesis of the 3-n-hexadecylpyrrole was carried out with a procedure as shown in scheme 1.



Scheme 1. Procedure for synthesis of 3-n-hexadecylpyrrole

The Langmuir-Blodgett films were prepared on a modified commercially available Lauda film balance. The subphase was purified water with 0.57 mg/2 mL C₁₆H₃₃-pyrrole and 0.98 mM CHCl₃. The monolayers were transferred to the substrates at a pressure of 20 mN/m. The substrates were ZnSe crystals

and Si wafers for transmission and Pt coated microscope slides for reflection. Good quality films could be made as indicated by a sharp rise in pressure with compaction.

Figure 5 shows the transmission spectrum (A) and the IRRAS spectrum (B) of five monolayers and the IRRAS spectrum of one monolayer (C) Langmuir-Blodgett films. For the five monolayer films, the N-H stretching mode, with dipole moment nearly parallel to the hydrocarbon tail, is clearly visible when the electric field vector is perpendicular to the substrate. This mode is absent in the transmission spectrum with the electric field vector parallel to the substrate. The polarization dependent intensity change of the 2954, 2962 and 2875 cm^{-1} C-H stretching modes can be seen more clearly in Fig. 6. The

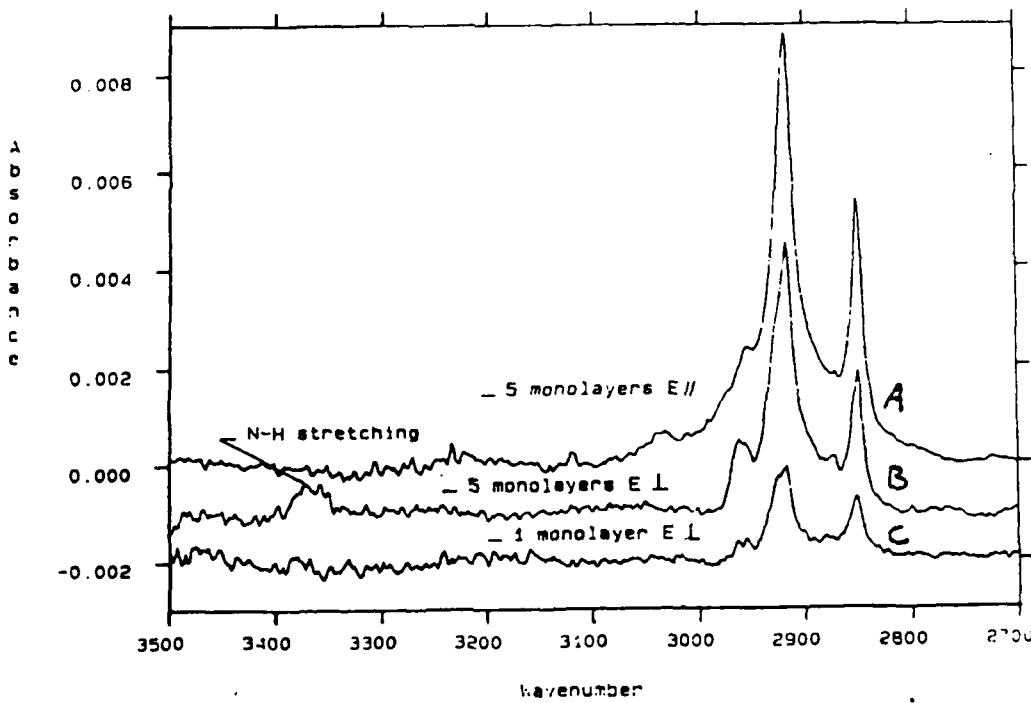


Fig. 5. FTIR spectra of $\text{C}_{16}\text{H}_{33}$ -pyrrole Langmuir-Blodgett films in the C-H and N-H stretching regions.
(A) Transmission of five monolayers on ZnSe
(B) IRRAS of five monolayers on Pt
(C) IRRAS of one monolayer on Pt

dipole moment of the CH_3 asymmetric stretching mode at 2962 cm^{-1} and the CH_3 symmetric stretching mode at 2875 cm^{-1} are parallel to the hydrocarbon tail, while the dipole moment of the CH_3 asymmetric stretching mode at 2954 cm^{-1} is perpendicular to the hydrocarbon tail. Comparing the spectra in (A) and (B) with the two orthogonal polarizations of the electric field vector, it can be concluded that the $\text{C}_{16}\text{H}_{33}$ -pyrroles are oriented close to normal to the substrate surface.

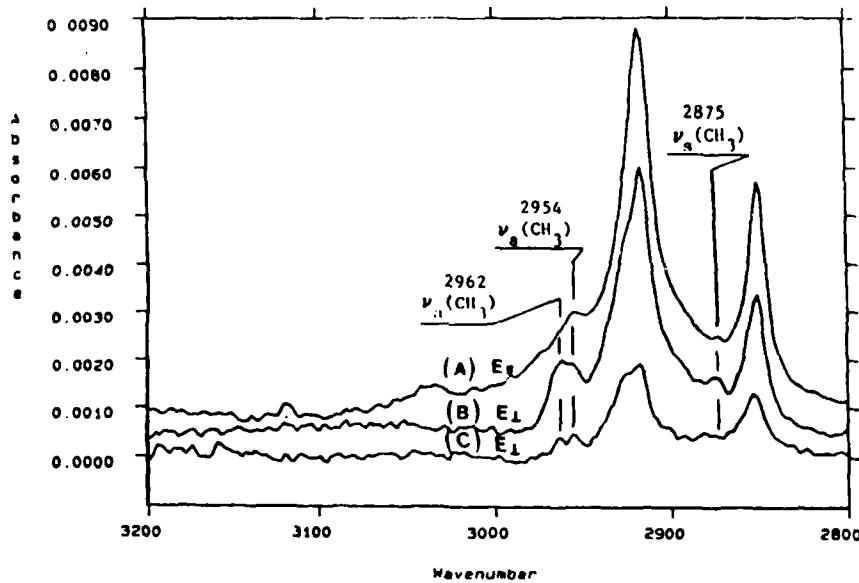


Fig. 6. FTIR spectra of $\text{C}_{16}\text{H}_{33}$ -pyrrole Langmuir-Blodgett films in the C-H stretching region.
 (A) Transmission of five monolayers on ZnSe
 (B) IRRAS of five monolayers on Pt
 (C) IRRAS of one monolayer on Pt

For a single monolayer, there is no predominance of either of the spectral features, suggesting that the $\text{C}_{16}\text{H}_{33}$ -pyrroles are tilted relative to the metal surface. This is likely due to interaction between the metal

surface and the π -electron cloud of the pyrrole head groups. The restrictions of the hydrocarbon tails prevent the pyrrole rings from lying flat on the Pt surface.

Steric restrictions prevent the formation of polypyrrole from $C_{16}H_{33}$ -pyrrole monomers by chemical oxidation with $FeCl_3$ on the water surface, since linear polypyrrole requires an alternating orientation of the pyrrole moieties. However, good polymer films could be made with a 1:1 ratio of $C_{16}H_{33}$ -pyrrole and unsubstituted pyrrole, suggesting that an alternating arrangement of the pyrrole moieties as required for polymerization to a linear chain is in fact taking place. Indications are that the structure of these polymer films is similar to the monomer films. Work is in progress to determine the details of the electronic properties and structural parameters of the polymerized films.

Summary

We have demonstrated that ordered thin films of oxidized polyheterocycles can be produced both with electrochemical growth and Langmuir-Blodgett film formation. Traditional electrochemical growth processes yield films which may be ordered in the neutral, or reduced, state but assume a disordered and amorphous structure upon intercalation of anions. However, by manipulating the electrochemical growth process by complexing with organic macrocyclic anions, it may be possible to grow structures which are ordered in the oxidized state as well.

The Langmuir-Blodgett technique provides an elegant method for a rational design of ordered structures of electroresponsive polymeric systems. It is anticipated that this will have important applications in a number of technologies which rely on optically and electrically active interfaces.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-76CH00016.

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